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Copper(II) Complexing Capacity of River Waters in the Urban Area

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Synopsis. Hourly variation of copper(II) complexing capacity (CuCC) of water samples from the Kiryu River in Gunma prefecture was investigated. From the stand point of complexing capacity, the present water samples could be classified into two types, that is, the daytime type and the nighttime one. Water samples belonging to the former type contained some ligands derived from human activity, and naturally occurring ligands were mainly found in water samples belonging to the latter. The estimation of stability constant for copper(II) complex in water samples was also carried out on the basis of a single ligand model.

Since bioavailability of a trace metal in natural waters is affected by its chemical form,[1] the speciation of a trace metal becomes more and more important in the environmental chemistry. However, in most water systems, the existence of a variety of naturally occurring ligands makes the equilibrium calculation difficult and the discrimination of a free metal ion from a metal associated with such a ligand is also a task of great difficulty. On the basis of the above situation, the concept "Complexing Capacity" has been introduced. In the case of copper(II) as a trace metal, copper(II) complexing capacity (CuCC) of a water sample is an ability of the sample to remove added copper(II) from the free ion pool.[2]

Various methods for the determination of the CuCC have been proposed and reviewed by Hart et al.[3,4] On the other hand, the authors have developed a back-extraction technique using bis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato) copper(II) $Cu(bfa)_2$ for the determination of CuCC,[5] and the proposed method was applied to river waters in the present work.

Experimental

A Shimadzu Model AA-670 atomic absorption/flame emission spectrophotometer equipped with a copper hollow cathode lamp (Hamamatsu Photonics) was used for copper determination. A Hitachi Model F-3010 fluorescence spectrophotometer was used for the determination of amino acids, and a Horiba Model F-16 pH meter was used for pH measurements. Total organic carbon (TOC) in sample solutions was determined with a Shimadzu Model TOC-500 total organic carbon analyzer, and analytical results were expressed by $\mu mol\,dm^{-3}$ for the sake of comparison.

Reagents. All the chemicals used were of guaranteed grade. Deionized water was used throughout.

Sampling Location. Water samples were collected on 6th of February, 1992 from the Kiryu River of Gunma Prefecture, and the sampling point was situated below Kiryu town.

Determination of Amino Acids. The determination of amino acids was carried out by the ninhydrin method,[6] and the results were expressed by $\mu mol\,dm^{-3}$ unit.

Determination of the CuCC. A water sample is filtered using a 0.45 μm membrane filter. Twenty cubic centimeters of the resulting sample is taken in a separatory funnel, and the equal volume of benzene containing 5.00×10^{-5} $mol\,dm^{-3}$ $Cu(bfa)_2$ is added. The mixture is shaken vigorously for 30 min. After the phases are allowed to separate, the aqueous phase is filtered, and copper(II) in the aqueous phase is determined with atomic absorption spectrometer. The CuCC value of a water sample is defined as the concentration of copper(II) back-extracted into the aqueous phase. The total concentration of a ligand $[L]_{tot}$ and stability constant for copper(II) complex β were estimated by modifying the above method,[5] in which back-extraction constant $K=3.02\times10^{-20}$ was used. This value was obtained from preliminary experiments in which nitrilotriacetic acid was adopted as a model ligand.

Table 1. Analytical Results of the Kiryu River Water Samples

Sampling time	pH	TOC	Amino acid	CuCC	$[L]_{tot}$	$\log\beta$
		$\mu mol\,dm^{-3}$	$\mu mol\,dm^{-3}$	$\mu mol\,dm^{-3}$	$\mu mol\,dm^{-3}$	
6:00	7.21	146	0.22	0.97	1.41	8.75
7:00	7.19	106	0.46	0.91	1.12	8.95
8:00	7.29	132	0.35	0.84	1.06	8.80
9:00	7.36	61	0.57	0.84	0.89	9.70
10:00	7.49	82	0.32	1.08	1.41	9.37
12:00	7.67	304	0.17	1.78	2.24	9.90
14:00	8.33	326	0.14	1.51	1.58	10.5
16:00	8.65	500	0.14	1.96	2.37	9.95
18:00	7.65	782	0.19	1.62	1.78	9.77
19:00	7.57	540	0.06	1.51	1.78	9.65
20:00	7.48	484	0	1.43	1.78	9.52
21:00	7.35	509	0.07	1.63	2.51	9.20
22:00	7.34	390	0.17	1.72	2.00	9.67
24:00	7.30	208	0.04	1.53	1.88	9.60

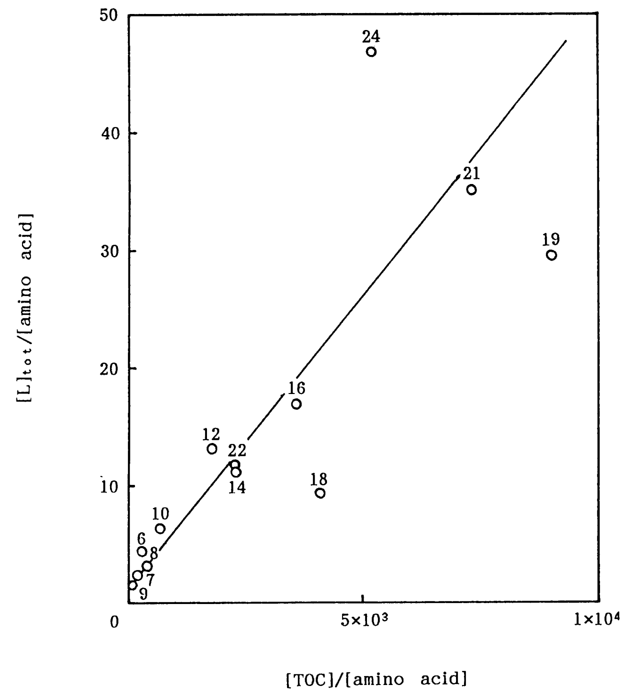

Fig. 1. Plot of $[\mathrm{L}]_{\mathrm{tot}}[\text{amino acid}]^{-1}$ against $[\mathrm{TOC}][\text{amino acid}]^{-1}$.
The number given in figure shows sampling time.

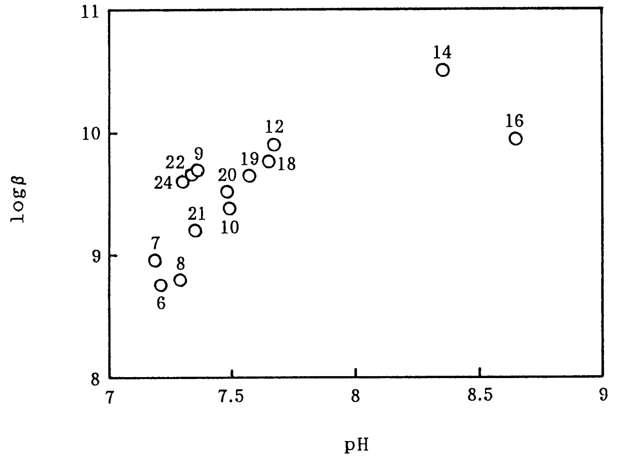

Fig. 2. Relationship between pH and log β value.
The number given in figure shows sampling time.

Results and Discussion

Analytical results of water samples are given in Table 1. Water samples taken in daytime tend to show rather higher pH compared with those obtained during nighttime, namely, water samples can be roughly classified into two types. As is seen in Table 1, higher pH value seems to correspond to lower amino acid concentration, while TOC tends to increase with increasing pH. Judging from sampling time, major part of TOC may depend upon human activities and amino acid may be derived from naturally occurring matter. A plot of $[\mathrm{L}]_{\mathrm{tot}}$ $[\text{amino acid}]^{-1}$ against $[\mathrm{TOC}]$ $[\text{amino acid}]^{-1}$ shown in Fig. 1, falls on a straight line although some deviations are seen. The straight line can be expressed by an equation; $[\mathrm{L}]_{\mathrm{tot}}[\text{amino acid}]^{-1}=0.005[\mathrm{TOC}][\text{amino acid}]^{-1}+1$, accordingly $[\mathrm{L}]_{\mathrm{tot}}=0.005[\mathrm{TOC}]+[\text{amino acid}]$.

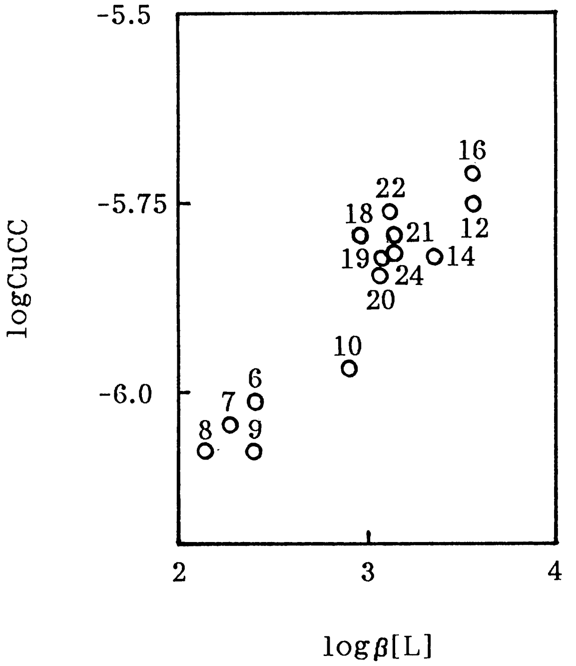

Fig. 3. Relationship between log β[L] value and log CuCC value.
The number given in figure shows sampling time.

The above relation indicates that TOC and amino acid act as ligands having complexing capacity to copper(II). Precisely speaking, ligands influencing the CuCC consist of a minute part of TOC and an amino acid. This means that most of [TOC] may be originated separately from the amino acids. However, the kind of amino acid cannot be specified at the present time. As is seen in Fig. 2, the log β tends to increase toward the high pH region. This phenomenon can be explained by assuming that the conjugate acid of a ligand is relatively weak, which dissociates along with the increasing pH. Therefore the β value estimated is a conditional stability constant. The concentration of free ligand [L] can be calculated by using the equation: $[\mathrm{L}]=[\mathrm{L}]_{\mathrm{tot}}-\mathrm{CuCC}$.

The experimental results enable us to estimate the log β [L], which is a measure of coordination ability of a ligand toward Cu^{2+}. The CuCC is closely related to log β[L] (Fig. 3), namely relative coordinating ability of a ligand can be estimated by the CuCC measurement.

References

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